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Dy_2O_3掺杂对机械球磨$Nd_2Fe_{14}B/\alpha$-Fe复合磁体矫顽力的影响*

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摘 要 用机械球磨法制备$Nd_2Fe_{14}B/\alpha$-Fe复合磁体，研究了Dy_2O_3掺杂对纳米复合磁体磁性能的影响。结果表明，掺入Dy_2O_3能显著提高复合磁体的矫顽力，且随着Dy_2O_3掺杂量的增大最大矫顽力对应的退火温度降低。X射线衍射分析结果表明，掺入Dy_2O_3使$Nd_2Fe_{14}B$的晶格常数减小，也即Dy部分替代Nd后生成了$(Nd, Dy)_2Fe_{14}B$硬磁相。因此，复合磁体矫顽力的增强主要归因于硬磁相磁晶各向异性的提高。但是，硬磁相磁晶各向异性的提高缩短了有效交换耦合长度，表现为过量掺杂Dy_2O_3使矫顽力降低。

关键词 金属材料，$Nd_2Fe_{14}B/\alpha$-Fe，Dy_2O_3掺杂，矫顽力，交换耦合

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Influence of Dy_2O_3 Doping on Coercivity of Mechanically Milled $Nd_2Fe_{14}B/\alpha$-Fe Composite Magnets

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ABSTRACT $Nd_2Fe_{14}B/\alpha$-Fe composite magnets were fabricated by mechanically ball milling. The influence of Dy_2O_3 doping on the coercivity of the nanocomposite magnets was studied in detail. It was found that the coercivity of the composite magnets can be significantly improved by Dy_2O_3 doping, and the annealing temperature corresponding to the maximum coercivity decreases with the increase of Dy_2O_3 content. X-ray diffraction analysis shows that the lattice parameters of $Nd_2Fe_{14}B$ decreased due to Dy_2O_3 doping, indicating that $(Nd, Dy)_2Fe_{14}B$ hard magnetic phase formed after Dy partial replacement for Nd. Therefore, the enhancement of coercivity of the magnets can be mainly attributed to the increase of the magnetic crystalline anisotropy of the hard magnetic phase. However, with the increase of the magnetic crystalline anisotropy, the effective exchange coupling length was shortened, thereby, the coercivity dropped due to over doping of Dy_2O_3.

KEY WORDS metal material, $Nd_2Fe_{14}B/\alpha$-Fe composite magnet, Dy_2O_3 doping, coercivity, exchange coupling

Nd-Fe-B系永磁材料具有高矫顽力和最大磁能积，得到了广泛的应用[1]。自Skomski和Coey等指出纳米双相复合磁体的理论磁能积可达1 MJ/m^{3}以来[2]，人们对纳米复合磁体进行了大量研究。但是，实际制备出的复合磁体在两相复合过程中矫顽力大幅度下降，导致其磁能积远低于理论值[3-8]。因此，关于复合磁体的研究主要集中在提高其矫顽力[9-11]。

Xu等[12]研究了DyF_3在Nd-Fe-B烧结磁体中的扩散，对晶粒及晶界的微结构分析发现，Dy部分替代Nd形成$(Nd, Dy)_2Fe_{14}B$并出现了Nd-O晶界相。这削弱了硬磁相之间的交换耦合作用，从而使磁体的矫顽力显著提高。但是，F^-离子的强腐蚀性降低

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了磁体的抗腐蚀性。Cui 等[13]报道, 在Nd-Fe-B烧结磁体中掺入Dy_2O_3可提高其抗腐蚀性能。此外, 在Nd-Fe-B磁体中掺杂氧化物可提高磁体的电阻率, 有利于提高其高频性能[14]。Fan 等[7]研究了掺杂稀土Nd对纳米复合磁体$Nd_2Fe_{14}B/\alpha$-Fe矫顽力的影响, 观察到掺杂稀土Nd可改善其微观结构, 提高矫顽力。本文用机械球磨及后续退火处理制备$Nd_2Fe_{14}B/\alpha$-Fe复合磁体, 研究掺杂Dy_2O_3对矫顽力的影响。

1 实验方法

实验用材料为30−115 μm 的$Nd_{11.1}Fe_{81.6}Zr_{1.4}B_{5.9}$粉(简记为NdFeB)、还原铁粉(99.99%)以及Dy_2O_3粉末。实验原料的配比为: NdFeB(4.8 g)+Fe(1.2 g)+xDy_2O_3 (x为质量百分比, x=0、1%、3%、5%和7%)。实验中使用GN-2型行星式高能球磨机, 转数为700 r/min, 按约16∶1的球料比在氩气气氛下机械球磨5 h。将球磨后的粉料在高真空(1.3×10^{-3} Pa)条件下退火10 min, 退火温度为893−1053 K。

用MSAL-XD2型X-ray衍射仪(Cu-K_α, λ = 0.15406 nm)分析样品的相组成。将0.02 g退火磁粉混入酚醛树脂中做成直径约2 mm厚度为4 mm的样品。用LakeShore 7404 Mode振动样品磁强计和Quantum Design Versa-lab振动样品磁强计测量样品的磁性, 最大外加磁场分别为1.8 T和3.0 T。对所有磁滞回线进行退磁修正, 退磁因子为0.28 [15]。

2 结果和讨论

图1给出了掺杂不同质量比Dy_2O_3的复合磁体在973 K退火后的XRD图谱。由图1可见, 样品主要含软磁相α-Fe和硬磁相$Nd_2Fe_{14}B$。依据XRD图谱计算了复合磁体中硬磁相$Nd_2Fe_{14}B$晶格常数, 结果列于表1。掺杂Dy_2O_3后硬磁相的晶格参数呈现了减小的趋势, 晶格常数c值持续变小。由此可以推断, 掺杂后Dy部分进入硬磁相晶格替代了稀土元素Nd, 其晶格参数减小趋势也符合镧系收缩的规律[16]。

图2给出了各掺杂量复合磁体矫顽力随退火温度的变化曲线。由图2可见, 无掺杂及掺杂1% Dy_2O_3样品的矫顽力随着退火温度的提高而持续增加, 在所研究的温度范围内未观察到获得最大矫顽力的退火温度。进一步增加Dy_2O_3掺杂量(质量分数)到x=3%、5%, 样品在1013 K退火时矫顽力最大。掺杂量增加到x=7%, 出现最大矫顽力的退火温度降低至973 K。在退火温度相同的情况下, 掺杂Dy_2O_3有利于提高复合磁体的矫顽力。掺杂量为3%、5%时, 矫顽力的提高幅度较大。掺杂量为7%、退火温度为1053 K时样品的矫顽力急剧下降, 且低于掺杂量为3%的样品。

图3给出了不同Dy_2O_3掺杂量的复合磁体在

表1 掺杂不同量Dy_2O_3的复合磁体973 K退火后的晶格常数

Table 1 Lattice parameters of composite magnets annealed at 973 K

x /%	a /nm	c /nm	V_{cell} /nm^3
0	0.8779	1.2176	0.9383
1	0.8782	1.2165	0.9382
3	0.8719	1.2140	0.9230
5	0.8697	1.2098	0.9152
7	0.8727	1.2088	0.9206

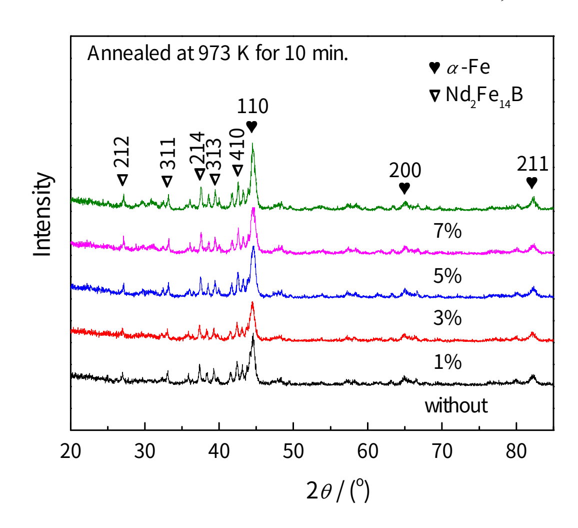


图1 不同Dy_2O_3掺杂量的复合磁体973 K退火后的XRD图谱

Fig.1 X-ray diffraction patterns of the composite magnets annealed at 973 K

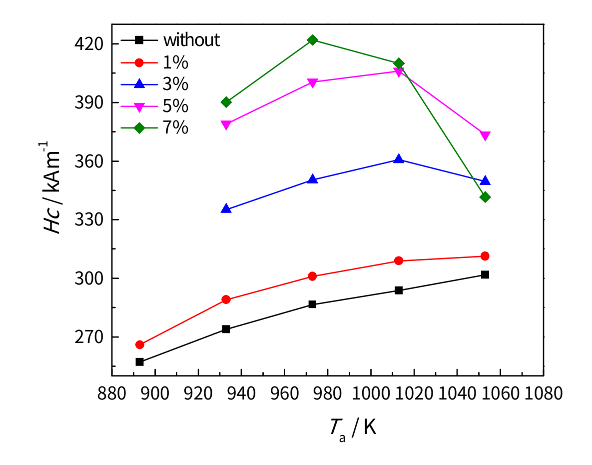


图2 不同Dy_2O_3掺杂量的复合磁体的室温矫顽力与退火温度的关系

Fig.2 Coercivity of composite magnets varying with the annealing temperature (measured at room temperature)

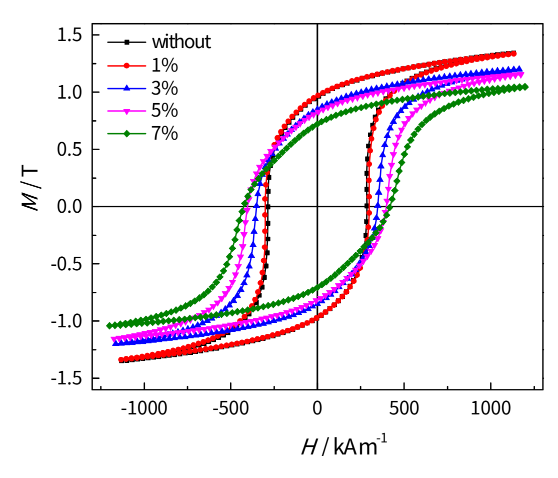


图3　不同Dy_2O_3掺杂量的复合磁体973 K退火后的磁滞回线

Fig.3 Hysteresis loops of composite magnets annealed at 973 K (measured at room temperature)

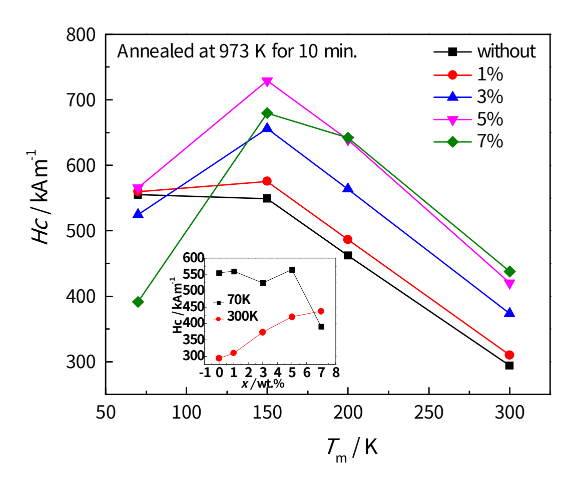


图4　不同Dy_2O_3掺杂量的复合磁体退火后的矫顽力与测量温度的关系, 内插图为在70 K和300 K测得的矫顽力与Dy_2O_3掺杂量的关系

Fig.4 Relationship between coercivity of composite magnets and measuring temperatures (70 K−300 K), the coercivity of composite magnets varying with the content of Dy_2O_3 at 70 K and 300 K, inset

973 K退火后的室温磁滞回线。相比于未掺杂样品, 加入Dy_2O_3后样品的饱和磁化强度和剩余磁化强度均降低, 且在设计的掺杂量范围内, 掺入量越大其饱和磁化强度和剩余磁化强度降低幅度越大。同时, 掺杂样品的矫顽力比未掺杂样品矫顽力有所提升, 且随着Dy_2O_3掺杂量的增加矫顽力持续升高。

由于软/硬磁相的交换耦合作用, 复合磁体呈现出单相的磁化行为。考虑到软磁相的平均软化效应, 交换耦合长度可表达为

$$L_{ex} = \sqrt{\frac{A_{eff}}{K_{eff}}} \qquad (1)$$

其中A_{eff}为有效交换常数, K_{eff}为有效磁晶各向异性常数。其中有效磁晶各向异性常数K_{eff}主要取决于硬磁相的磁晶各向异性和软磁相的含量[7]。由于Dy部分替代Nd形成了各向异性场高于$Nd_2Fe_{14}B$的$(Nd, Dy)_2Fe_{14}B$, 导致交换耦合长度减小。掺杂量越多复合磁体的有效磁晶各向异性越大, 交换耦合长度减少越多。尽管升高退火温度可为Dy替代Nd提供动力, 但是也促进晶粒长大。提高退火温度促进Dy替代Nd, 从而使矫顽力随掺杂Dy_2O_3量增加而升高; 继续提高退火温度使晶粒长大且交换耦合长度减少, 从而削弱交换耦合作用。因此, 在图2中出现最大矫顽力对应的退火温度随着掺杂量的增加而降低的现象。同时也观察到, 掺杂量x=7%时硬磁相磁晶各向异性的提高缩短了交换长度, 导致第二象限的磁滞回线具有更低的矩形度。

为了进一步分析硬磁相/软磁相之间的交换耦合作用, 测量了不同样品的低温磁性能。图4给出了掺杂不同量Dy_2O_3的复合磁体的矫顽力随测量温度的变化曲线。可以看到, 随着测量温度的降低样品的矫顽力先持续增加, 而当测量温度低于150 K时所有样品的矫顽力均降低, 也即$Nd_2Fe_{14}B$主相发生了自旋再取向[17]。由图4的插图可见, 测量温度为300 K时样品的矫顽力随着Dy_2O_3掺杂量的增加而越大, 尤其是掺杂量为3%和5%时矫顽力增加显著。但是测量温度为70 K时, 没有显示出明显的对应关系。尤其是Dy_2O_3掺杂量为7%的样品, 其矫顽力急剧降低; 尽管其室温矫顽力最高, 但是测量温度为70 K时其矫顽力最低。由公式(1)可知, 在低温下硬磁相磁晶各向异性增强缩短了交换耦合长度, 削弱交换耦合作用, 导致低温下矫顽力随Dy_2O_3掺杂量的提高变化不明显, 甚至在掺杂量为7%时矫顽力急剧降低。

3 结　论

对于用机械球磨法制备的$Nd_2Fe_{14}B$/α-Fe复合磁体, 掺入Dy_2O_3可提高其矫顽力, 且室温矫顽力随着Dy_2O_3掺入量(1%−7%)的提高而增大; 复合磁体的矫顽力随着退火温度的提高先增大后减小, 最大矫顽力对应的退火温度随着Dy_2O_3的掺入向低温移动。由于Dy替代Nd生成了硬磁性能更高的$(Nd, Dy)_2Fe_{14}B$相, 从而使矫顽力提高。但是磁晶各向异性的提高使交换长度缩短, 削弱硬磁相/软磁相交换耦合作用, 从而导致因掺杂Dy_2O_3而复合磁体低温矫顽力提高得不明显。

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